Fe adatoms along Bi lines on H/Si(001): Patterning atomic magnetic chains

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The stability, electronic and magnetic properties of Fe atoms adsorbed on the self-assembled Bi-lines nanostructure on the H/Si(001) surface are addressed by spin-density functional calculations. Our results show that Fe adatoms are much more stable on sites closer to the Bi nanolines, suggesting that they form one-dimensional atomic arrays. The most stable structure occurs on a missing dimer line beside the Bi dimers, which corresponds to an array with distances between Fe adatoms of about 8 Å. In this array the irons are coupled antiferromagnetically with spin magnetic moment of about 1.5 μ_B per Fe atom, whereas the coupling exchange interactions is found to be of 14.4 meV. We also estimate a large magnetic anisotropy energy of about 3 meV/atom originated on the structural anisotropy of the Fe-adatom site. In addition, we find that the electronic band structure of the Fe array at the most stable structure shows a magnetic half-metal behavior.

Self-organized nanostructures on surfaces have attracted much attention during the last few years owing their promising applications in the patterning of low-dimensional magnetic systems [1]. Suitable epitaxial techniques make possible to build one-dimensional (1D) arrays of $3d$ magnetic atoms by step decoration of metallic substrates, which is currently a very active topic of research in magnetism from both experimental [2, 3, 4] and theoretical [5, 6] viewpoint. New fundamental physical phenomena like magnetic ordering and giant magnetic anisotropy have been observed in self-assembly 1D arrays of magnetic atoms [7]. On the other hand, little is known about the spin interactions of magnetic atoms in contact with semiconducting surfaces. Recently, thin films of magnetic transition metal on Si(001) have been studied from first principles by Wu *et al.* [8]. They found that MnSi films on Si(001) are ferromagnetic with sizable magnetic moment, whereas FeSi and NiSi are nonmagnetic. Following up on earlier studies of magnetism in monoatomic arrays grown by self assembly on metallic substrates, we explore similar magnetic arrays on semiconducting surfaces taking advantage on the remarkable structural quality of the self-assembled Bi-dimer lines on the Si(001) surface. These nanolines, which are obtained by Bi deposition onto Si(001) above the desorption temperature of 500 °C, consists of two parallel rows of symmetric Bi dimers which are about 0.6 nm apart and can be over 500 nm in length. Additionally, their structures are free of defects like kinks or breaks and have a remarkable straightness [9, 10, 11]. However, possible template applications require the hydrogen exposure of the Si(001) substrate, since it is more reactive than the Bi line. After hydrogenation of Bi/Si(001), the H atoms only terminate the Si ones leaving the Bi lines clean and preserving their 1D structures [9, 12]. Recently, the arrengement of non-magnetic atoms on the Bi-nanolines structure as well as their use as a template have been experimentally investigated [13, 14, 15].

In this work we explore the possibility to construct magnetic monoatomic chains of Fe adatoms by decoration of self-assembled Bi lines on H/Si(001) surfaces. We find that the Fe adatoms have the most-stable structure beside the Bi-dimer, forming nearly 1D atomic arrays following the Bi-dimer lines with a Fe-Fe distance of about 8 Å. The Fe adatom array in the most stable configuration is antiferromagnetic, having a weak exchange coupling of 14.4 meV, suggesting the formation of extremely narrow magnetic domain walls. We also estimate a lower limit for the magnetic anisotropy energy (MAE) which is the energy involved in rotating the magnetization from a direction of low energy toward one of high energy. We find a very large MAE of about 3 meV/atom, which suggest a relatively high energy barrier to change the magnetization from preferential directions. Concerning the electronic properties, the 1D Fe array shows a magnetic half-metal behavior, i.e., the majority-spin electrons are semiconducting whereas the minority-spin electrons are metallic. The above results turn the Fe arrays on Bi lines an interesting system both for basic research and for possible technological applications, for instance in spintronics and nanoscale data-storage devices. We hope that experimental studies will be motivated by our predictions.

The calculations were performed in the framework of the density functional theory within the local-spin-density approximation (LSDA) [16], considering non-collinear magnetic ordering as implemented in the SIESTA code [17]. The basis set consists of numerical pseudoatomic orbitals, namely, double-ζ plus polarization functions. Standard norm-conserving pseudopotentials in their separable form were used to describe the electron-ion interaction, including nonlinear core correction for Fe and Bi atoms [19]. Currently, there are two energetically favorable structural models to explain the observed self-assembled Bi-dimer lines on clean and hydrogenated Si(001) substrates. These are the Miki[10] and the Haiku[11] structures. We adopt the latter one because it exhibits the highest stability on H/Si(001) as recently shown by *ab initio* calculations [18]. To simulate the Bi lines in the Haiku model structure we used the repeated slab method within a 2×6 surface unit cell, containing ten monolayers of Si atoms plus a vacuum region of about 11 Å. The bottommost Si dangling bonds

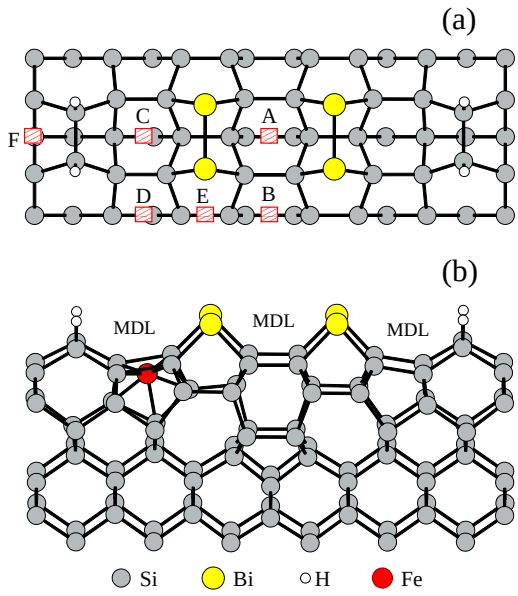

FIG. 1: (Color on line) (a) Top view equilibrium geometry for the clean Bi line on H/Si(001). Dashed squares indicate the Fe adsorption sites under consideration. (b) Most stable equilibrium geometry resulting from the Fe adsorption on the site C.

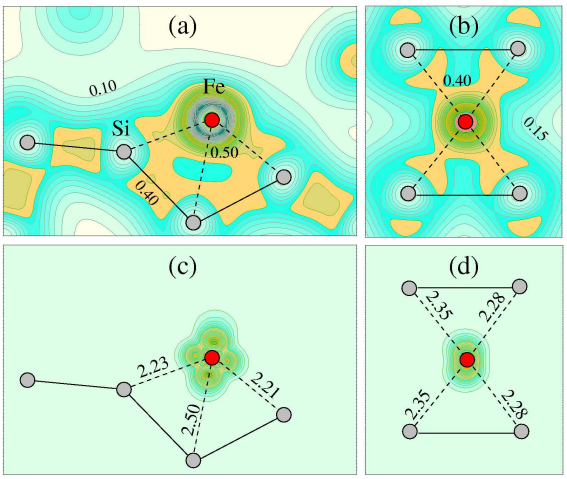

FIG. 2: (Color on line) (a) and (b) Total charge density on a plane perpendicular to the Bi dimers passing by the Fe atom, and through a plane passing by the topmost four Si atoms nearest neighbors to the Fe atom, respectively. (c) and (d) show the magnetization through the same planes than (a) and (b). Numbers in the upper panel correspond to the contour charge density in $e/\text{Å}^3$, and those of the lower panel correspond to bond lengths in Å.

were saturated by hydrogens. Four special $k_{\|}$ points were used to sampling the surface Brillouin zone. The topmost eight monolayers were fully relaxed until the force components become smaller than 0.05 eV/Å.

We investigate six adsorption sites for the Fe atom on the Bi-dimer structure formed on the hydrogenated Si(001) substrate (hereafter the clean Bi line), as shown in Fig. 1(a). In the clean Bi line, two parallel Bi dimers align along the [110] direction which are separated by a missing dimer line (MDL). In Addition, two adjacent MDLs form beside the Bi dimers. The Bi-dimer bond lengths and the lateral distance between them are found to be 3.15 and 6.36 Å, respectively. Our results for the equilibrium geometry of the clean Bi line is in good agreement with previous plane-waves *ab initio* results [18].

Figure 1(b) shows the equilibrium geometry for the most stable structure of the Fe adatom at the MDL beside the Bi dimers (C site). We find that the Fe atom tends to increase the number of Fe-Si bonds occupying an interstitial subsurface position, about 0.5 Å below the topmost Si atoms, becoming sevenfold coordinated with bond lengths ranging from 2.2 to 2.5 Å. Similar coordination numbers are found for the Fe adsorption on the other sites. The binding energy of the Fe adatom on the C site is found to be about 6 eV. These results somewhat mimic the B20 phase of FeSi iron silicide. The Fe atoms in FeSi (B20) have seven nearest-neighbor Si atoms, and binding energy of 6.58 eV, obtained by LSDA calculations [20]. Table I shows relative total energies for the Fe adatom at each sites. We note that the Fe adatom on sites A, B, and D are close in energy that the most stable one. This suggests that the MDLs are the energetically favorable positions for the Fe adsorption. On the other hand, Fe adatom between Bi dimers of the same line and on the hydrogenated Si(001) far from the Bi dimers, sites E and F respectively, are 0.82 and 1.07 eV higher in energy. At the E site, the Fe adatom breaks the Bi dimers, forming two Fe–Bi bonds with lengths of 2.58 Å and four Fe–Si bonds with lengths of 2.2 and 2.7 Å. This is the only case where the Bi dimers break. We also find that all Fe adatom structures are magnetic with magnetic moment ranging from 1.5 to 2.0 μ_B per Fe atom. The above results suggest that the Bi lines would be effective to adsorb Fe atoms, supporting the proposed formation of 1D magnetic arrays. It is important to note that the energetic preference for the adsorption sites A to D indicates that the Bi-line structure would not be destroyed by the Fe adsorption.

Figures 2(a) and 2(b) show total charge densities for

TABLE I: Total energy (ΔE) with respect to the most stable structure (C site), binding energy (E_b) of the Fe adatom and spin magnetic moment (m) of ferromagnetically coupled Fe arrays. CN is the Fe-adatom coordination number.

Sites	ΔE (eV)	E_b (eV/Fe)	m (μ_B/Fe)	CN
A	0.134	5.834	1.83	6
B	0.350	5.618	1.63	6
C	0.000	5.968	1.53	7
D	0.120	5.848	1.27	7
E	0.816	5.152	1.99	8
F	1.072	4.896	1.95	7

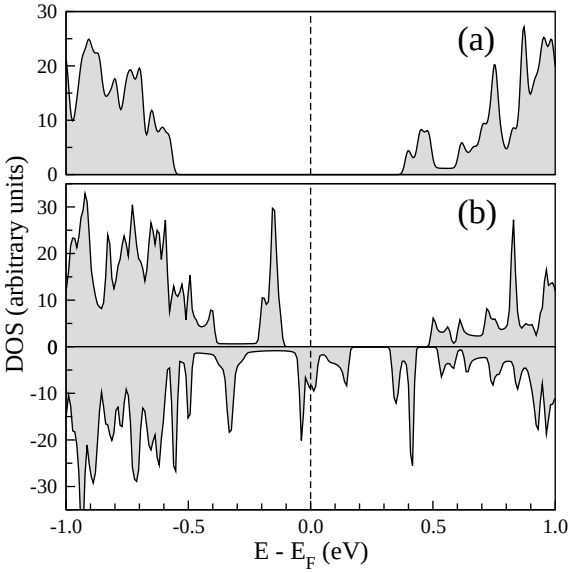

FIG. 3: (a) Density of states (DOS) for the clean Bi line on H/Si(001). (b) Spin-resolved DOS for the Fe adatom on the Bi lines at the most stable structure.

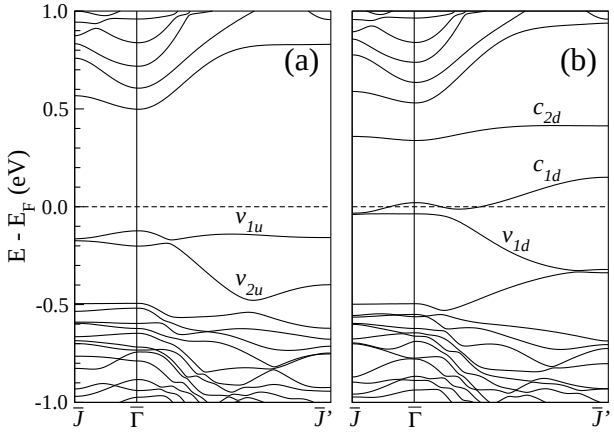

FIG. 4: Electronic band structure for the Fe adatom on the Bi lines at most stable structure. (a) and (b) indicate the majority and minority spin bands, respectively.

the Fe adatom on the site C on planes perpendicular to the Bi dimers passing by the Fe atom, and parallel to the surface passing by the topmost four Si atoms nearest neighbors to Fe, respectively. Here we see that the iron binds with their seven silicon nearest neighbors, forming metallic bonds. Typically, pairs of Fe-Si bonds have same lengths whereas an extra one is longer, showing a highly anisotropic environment. Similar results are found for the other Fe adsorption sites. High-coordinated Fe adatoms at subsurface has been also verified in several studies addressing the formation of iron silicide thin films on Si(001) [8, 21] and Si(111) [22, 23].

In Figure 3(a) we present the calculated density of states (DOS) for the clean Bi line on H/Si(001). We find that this system is semiconducting exhibiting an energy gap of about 1 eV. The occupied Bi states lie resonant close to the top of the valence band, whereas the electronic states attributed to the Si-dimer dangling bonds are suppressed by the hydrogen saturation, opening the energy gap. Figure 3(b) shows the spin-resolved DOS for the Fe adatom on the Bi line in the most stable structure, which reveals different electronic properties for each spin channels. While the majority spin exhibits a semiconducting character, the minority spin appears to be metallic. In order to elucidate these findings, we plot the electronic band structure for both majority and minority spin channels, as shown in Figs. 4(a) and 4(b), respectively. In these figures, the $\bar{\Gamma}\bar{J}'$ ($\bar{\Gamma}\bar{J}$) direction corresponds to wave vectors parallel (perpendicular) to the Bi lines. It is worthy to note that the gap states dispersion along $\bar{\Gamma}\bar{J}$ are rather artificial, originating in the supercell construction. The distance between neighboring Bi lines in our calculation is about 17 Å, however the experimentally observed are much more separated. We find that the electronic states v_{1u}, v_{2u}, v_{1d}, and c_{2d} come from the $3d$ orbitals of Fe adatom, with negligible contribution from Si and Bi atoms. The spin-resolved density of states for the structural model C, Fig. 3(b), indicates that the net magnetization of Fe arrays comes mainly from the electronic states induced by Fe adatoms at $E_F - 0.15$ eV (v_{1u}), with a small contribution from the electronic states lying at $E_F - 0.4$ eV (v_{2u}). On the other hand, the minority spin density exhibits two peaks, one at $E_F - 0.32$ eV, and another one crossing Fermi level. The latter contribution comes from v_{1d}+c_{1d}, see Fig. 4(b). We observe that the c_{1d} state gives a semimetallic character in the minority spin channel along the Bi line, however, the majority spin channel behaves as a semiconductor with a bandgap of about 0.6 eV. This behavior, known as magnetic half metals, was initially predicted by band structure calculations in Heusler alloys [24]. Similar magnetic half-metal behavior is found for the Fe adatom at the A site. However, for the Fe adatom at the B and D sites, both spin channels have a metallic character. The above results also suggest that Fe adatoms on Bi lines would be a reliable system for spin injection from a ferromagnetic material into a semiconductor. According to our results, if an spin-polarized current is successfully injected into the most stable Fe array, only one spin channel would be able to initiate de conduction.

Figures 2(c) and 2(d) show contour plots for the net magnetization, defined as $m(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r})$, where $\rho_\uparrow$ and $\rho_\downarrow$ represents the total charge density for the majority and minority spin channels, respectively. In order to establish the strength of magnetic coupling (J) we calculate the difference in energy of the ferromagnetic (FM) and antiferromagnetic (AFM) ordering by doubling the supercell size. Our results show that the Fe adatoms at the C site are coupled antiferromagnetically with a weak exchange interaction of $J = 14.4$ meV. The presence of nonmagnetic Si substrate intermediating the Fe adatoms suggests a superexchange origin for the AFM coupling.

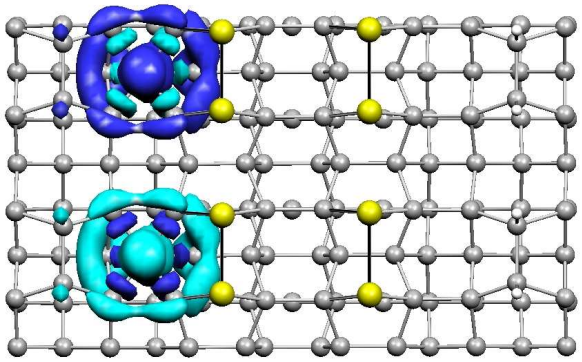

FIG. 5: (Color on line) Isosurfaces of the antiferromagnetic magnetization induced by the Fe adatoms along the Bi lines in the most stable structure. The clear (dark) isosurfaces correspond to the majority spin (minority spin) density of $+0.004$ (-0.004) $e/\text{Å}^3$.

Figure 5 shows isosurfaces of the AFM magnetization calculated within the double supercell scheme. We observe that the Fe adatom polarizes with an opposite spin density the electronic charge between the Si-Fe bonds. The only atoms which are effectively polarized are the hydrogens nearest neighbors. Magnetic moments of the ferromagnetically coupled Fe atoms in the different adsorption sites are shown in Table I. We note that the highest magnetizations occur for the configuration E. Here, the Fe adatom binds with the Bi atoms, breaking the dimer. This suggests that the increased magnetization are due to the polarization of the Bi atoms which contribute with additional electrons when forming the Fe-Bi bonds. For the Fe adsorption on the H-saturated Si dimers, site F, we find a magnetic moment of 1.95 μ_B per Fe atom, in close agreement with a previous calculation [25].

We find that the structural anisotropy of the Fe adatom site induces a magnetic anisotropy which would be originated in local magnetic dipolar interactions. We estimate a lower limit for the magnetic anisotropy energy by taking the difference in energy for the spin magnetization pointing in a direction of low energy (easy axis) toward one of high energy (hard axis). By non-collinear spin calculations we find that the easy axis occurs at $\theta \approx 0°$ and $\theta \approx 117°$, whereas the hard axis occurs at $\theta \approx 50°$, where θ is the azimuth angle. In both cases, the magnetization vector is parallel to the Bi dimers. We find a very large MAE of about 3 meV/atom without considering spin-orbit contributions, which are not included in the present calculations. Although the orbital moment would be important for the magnetic anisotropy of adatoms on metallic surfaces, for instance Co adatom on Pt(111) [7], it would be small or even quenched for Fe adatom on the Bi-lines structure due to its enhanced coordination, which resembles a bulk-like environment.

In summary, we have examined the stability, electronic and magnetic properties of Fe atoms adsorbed on the neighborhood of the Bi-dimer nanolines on H/Si(001), using spin-density functional calculations. Our results show that the Fe atoms tend to occupy highly coordinated subsurface position beside the Bi lines, suggesting the formation of nearly 1D atomic arrays. At the most stable configuration the Fe array couples antiferromagnetically with a weak exchange coupling of 14.4 meV. We estimate a large magnetic anisotropy energy for a single Fe adatom of about 3 meV/atom, suggesting a relatively high energy barrier to change the magnetization from the preferential directions. In addition, the electronic band structure of the most stable Fe array shows a magnetic half-metal behavior for the spin channels. Considering that Bi nanolines on Si(001) is currently grown by self assembling, we have shown that its use as a pattern in the design of nearly 1D magnetic arrays is energetically favorable. Our results suggest possible applications in nanomagnetic devices as well as in spintronics, requiring complementary experimental investigations.

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